

高介電係數介電質在金氧金電容之研究

研究生：江國誠

指導教授：荊鳳德教授

國立交通大學

電子工程學系暨電子研究所

摘要

在各種不同的被動元件中，金氧金電容經常被廣泛的應用在電路裡的去耦合、阻抗匹配與直流濾波器中；而且它們通常佔據了很大比例的電路面積。此外金氧金電容也是發展高密度動態記憶體中面臨的重要挑戰。記憶體電容是決定檢測訊號電壓、速度還有防止軟件誤差影響資料保存時間和耐久性的重要參數。而根據國際半導體技術藍圖制定會 (ITRS)，為了元件尺寸縮微和節省成本，金氧金電容的面積必須不斷的減少。

因為減低電容的厚度會增加不必要的漏電流以及惡化電容變化係數，所以使用高介電常數的介電層是唯一的解決方法。此外技術的趨勢在於發展同一種高介電材料應用於類比、射頻和動態記憶體嵌入式系統單晶片。所以高介電材料應用在金氧金電容從氮氧化矽 ($\kappa \sim 4-7$)、氧化鋁 ($\kappa=10$)、氧化鉛 ($\kappa \sim 22$)、氧化鉭 ($\kappa \sim 25$) 一直發展到氧化鈮 ($\kappa \sim 40$)。但是目前在這些材料中還無法同時達到在高電容密度下金氧金電容所需要的特性，例如低電壓和低電容變化係數。因此在這裡，我們發展出新的製程和超高介電係數的材料來改進金氧金電容，例如氧化鈦和氧化鉭的混合物、氧化鈦和氧化鉛的混合物 ($\kappa \sim 45-50$) 與鈦酸鋇 ($\kappa \sim 50-300$)。為了進

一步改善這些介電質低能隙的缺點,應用高功函數鎳或鉍的上電極可得到較佳的特性。如此在有限的熱預算下,不只高電容密度和低漏電還有低電容變化係數都可以同時實現。

除了基本的漏電流與低頻量測以外,我們另外量測了射頻電容的高頻散射參數。並運用數學模擬軟體,萃取出元件在不同頻率所具有的電容大小。除此我們還深入研究電容的傳導機制與電容變化跟電壓和溫度相關的成因,一些重要的因素如介電質跟電極間的介面層、能障、和表面粗糙度還有相關材料特性都在這篇論文中透徹的討論,相信這對發展高特性金氧金電容會有很大的幫助。

The Investigation of Metal-Insulator-Metal

Capacitor Using High- κ as Dielectrics

Student: K. C. Chiang

Advisor: Dr. Albert Chin

Department of Electronics Engineering

& Institute of Electronics

National Chiao Tung University

Abstract

Among various passive devices, metal-insulator-metal (MIM) capacitors are widely used for decoupling, impedance matching and direct current (DC) filtering; they occupy a large fraction of circuit area. Moreover, one of the most critical challenges which gigabit density DRAM's face will be MIM memory cell capacitance. Memory cell capacitance is the crucial parameter which determines the sensing signal voltage, sensing speed, data retention times and endurance against the soft error event. According to International Technology Roadmap for Semiconductors (ITRS), continuous down-scaling of the size of MIM capacitors is required to reduce chip size and the cost.

To meet these requirements high dielectric constant (κ) materials provide the only solution, since decreasing the dielectric thickness (t_d) to increase the capacitance density degrades both the leakage current and $\Delta C/C$ performance. Furthermore, it is

also desirable to use the same high- κ dielectric to meet all the Analog, RF and DRAM functions for embedded SoC. Therefore the high- κ dielectrics used in MIM capacitors have evolved from SiON ($\kappa\sim 4-7$), Al₂O₃ ($\kappa=10$), HfO₂ ($\kappa\sim 22$), Ta₂O₅ ($\kappa\sim 25$) to Nb₂O₅ ($\kappa\sim 40$). However, the demonstration of MIM with these films is yet able to achieve properties such as nondispersive, good linearity and high breakdown with low leakage concomitantly, at high unit capacitance. Hence, we have developed novel process and very high- κ materials, such as TiTaO, TiHfO ($\kappa\sim 45-50$) and STO ($\kappa\sim 50-300$) to advance this technology. To further improve small bandgap (E_G) in these dielectrics, a high work-function (ϕ_B) Ir or Ni (5.2 eV) electrode is used to give better performance. Therefore, not only high capacitance density, and low leakage current, but also small voltage- and temperature- dependence of capacitance are achieved under limited thermal budget for back-end integration.

In addition to the measurements of leakage current density and capacitance at low frequency, we also measured the S-parameters to investigate the characteristics of the MIM capacitors at RF regime. Using the simulation software, the capacitance of the device at different frequencies was extracted. Moreover, understandings of the mechanism of conductivity, voltage- and temperature-dependence of capacitance were studied, which are also useful in the development of advanced MIM devices. The related factors, such as barrier height, surface roughness, interfacial layer, and

dielectric material properties should be concerned for improving MIM performance, which were also investigated in this thesis.

Acknowledgement

First, I would like to thank my advisor Prof. Albert Chin for his fruitful discussion and illuminative comment. I am also grateful to all ED633 group members, Dr. M. Y. Yang, Dr. C. C. Chen, Dr. H. L. Kao, Dr. B. F. Hung, C. H. Wu, Terry Wang, Z. W. Lin and W. L. Huang, for their enthusiastic assistance and cooperation. Moreover, I thank for my girl friend Miss Hsiao. Finally, I deeply appreciate my family and parents' endless encouragement and spiritual support. Without them, I can't finish this dissertation.

Contents

Abstract (in Chinese)	i
Abstract (in English)	iii
Acknowledgement	v
Contents	vi
Figure Captions	viii
Table Captions	xvi

Chapter 1 Introduction

1.1 Motivation to study MIM capacitors.....	1
1.2 Motivation to study MIM capacitors using high- κ dielectrics.....	4
1.3 The measurement of the devices.....	5
1.4 Innovation and contribution.....	6

Chapter 2 High- κ Ir/TiTaO/TaN Capacitors Suitable for Analog IC Applications

2.1 Introduction.....	12
2.2 Experimental.....	13
2.3 Results and discussion.....	13
2.4 Conclusion.....	16

Chapter 3 Very High Density ($23\text{fF}/\mu\text{m}^2$) RF MIM Capacitors Using High- κ TiTaO as the Dielectric

3.1 Introduction.....	21
3.2 Experimental.....	22
3.3 Results and discussion.....	23
3.4 Conclusion.....	25

**Chapter 4 Thermal Leakage Improvement by Using a High Work Function
Ni Electrode in High- κ TiHfO MIM Capacitors**

4.1 Introduction.....	30
4.2 Experimental.....	31
4.3 Results and discussion.....	32
A. <i>Electrical C-V & J-V characteristic</i>	32
B. <i>$\Delta C/C$ and $VCC \alpha$</i>	32
C. <i>Current conduction mechanism</i>	34
D. <i>Performance comparison</i>	36
5.4 Conclusion.....	37

**Chapter 5 High Performance SrTiO₃ Metal-Insulator-Metal Capacitors for
Analog Applications**

5.1 Introduction.....	46
5.2 Experimental.....	47
5.3 Results and discussion.....	48
A. <i>Electrical C-V & J-V characteristic</i>	48
B. <i>Current conduction mechanism</i>	50
C. <i>Material characterization</i>	51
D. <i>$\Delta C/C$, α, and TCC</i>	53
E. <i>Performance comparison</i>	55
5.4 Conclusion.....	55

**Chapter 6 Very High Density (44fF/ μm^2) SrTiO₃ MIM Capacitors for RF
Applications**

6.1 Introduction.....	69
6.2 Experimental.....	70

6.3 Results and discussion.....	71
6.4 Conclusion.....	74
Chapter 7 Use of a High Work-Function Ni Electrode to Improve the Stress Reliability of Analog SrTiO₃ Metal-Insulator-Metal Capacitors	
7.1 Introduction.....	80
7.2 Experimental.....	81
7.3 Results and discussion.....	82
7.4 Conclusion.....	85
Chapter 8 Conclusion and Recommendation.....	91
References.....	95
Vita.....	128
Publication List.....	129

Figure Caption

Chapter 1 Introduction

Fig. 1-1 The International Technology Roadmap of analog and mixed-signal capacitors.

Fig. 1-2 The measurement set-up for S-parameter.

Fig. 1-3 The illustration of HP85122A and ATN-NP5B noise measurement system.

Chapter 2 High- κ Ir/TiTaO/TaN Capacitors Suitable for Analog IC Applications

Fig. 2-1 C - V characteristics of Ir/TiTaO/TaN TiTaO MIM capacitors.

Fig. 2-2 (a) J - V characteristics of Ir/TiTaO/TaN MIM capacitors. (b) Band diagram of the Ir/TiTaO/TaN MIM structure. The leakage current is lower when electrons are injected from the top Ir electrode than from the lower TaN electrode.

Fig. 2-3 (a) $\Delta C/C$ - V and (b) $\Delta C/C$ - I/C plot for Ir/TiTaO/TaN MIM capacitors.

Chapter 3 Very High Density ($23\text{fF}/\mu\text{m}^2$) RF MIM Capacitors Using High- κ TiTaO as the Dielectric

Fig. 3-1 XRD patterns of TiO_2 and TiTaO dielectric layers, ~ 28 nm thick, after 400°C O_2 oxidation and N_2 annealing.

Fig. 3-2 (a) C - V and (b) J - V characteristics of TiO_2 and TaTiO capacitors. The leakage current is lower in the TiTaO capacitors.

Fig. 3-3 The scattering parameters of a TiTaO MIM capacitor, from 200 MHz to 20 GHz. Insert: the equivalent circuit model used for capacitance extraction.

Fig. 3-4 (a) The $\Delta C/C$ -V characteristics of a TiTaO MIM capacitor. The data for frequencies >1 MHz were obtained from the S-parameters. (b) Frequency dependent capacitance density, $\Delta C/C$, α and β for a TiTaO MIM capacitor biased at 2V.

Chapter 4 Thermal Leakage Improvement by Using a High Work Function Ni Electrode in High- κ TiHfO MIM Capacitors

Fig. 4-1 (a) Comparison of the band gap and band offset with various high- κ dielectrics (b) The possible high work-function metals in the Periodic Table.

Fig. 4-2 (a) C-V characteristics of [Ni or Al]/TiHfO/TaN capacitors, measured at various frequencies (b) J-V characteristics of [Ni or Al]/TiHfO/TaN capacitors measured at 25 °C and 125°C.

Fig. 4-3 (a) $\Delta C/C$ - V characteristics of [Ni or Al]/TiHfO/TaN capacitors and (b) J-V and $\Delta C/C$ -V (insert) for the Ni-based capacitors.

Fig. 4-4 $\log(J)$ versus $\log(E)$ plots of [Ni or Al]/TiHfO/TaN capacitors measured at 25 °C and 125°C

Fig. 4-5 Measured and simulated J - $E^{1/2}$ of (a) Al/TiHfO/TaN and (b) Ni/TiHfO/TaN

devices and inserted band diagrams under thermal equilibrium.

Fig. 4-6 (a) The Schottky Emission (SE) fitting of [Ni or Al]/TiHfO/TaN capacitor data at low electric field, and (b) the FP fits of a Ni/TiHfO/TaN capacitor data at high field. The related band diagrams are included.

Fig. 4-7 $\Delta C/C-I/C$ plots. An exponential decrease of α with increasing dielectric thickness was observed.

Chapter 5 High Performance SrTiO₃ Metal-Insulator-Metal Capacitors for Analog Applications

Fig. 5-1 (a) $C-V$ and (b) $J-V$ characteristics of TaN/STO/TaN MIM capacitors processed under various conditions. The 400°C PDA yields a capacitance density of 17 fF/ μm^2 which increases to 28 fF/ μm^2 for a 450°C PDA and is better with the N⁺ treatment (35 fF/ μm^2).

Fig. 5-2 (a) $J-V$ characteristics for the devices in Fig. 1 measured at 125°C. (b) Comparison of the $C-V$ and $J-V$ characteristics of TaN/STO/TaN MIM capacitors.

Fig. 5-3 $J-V$ and $C-V$ (insert) characteristics of an STO MIM capacitor using the optimum process conditions.

Fig. 5-4 Plot of $\ln(J)$ versus $E^{1/2}$ under electron injection from (a) the lower and (b) the top electrode.

Fig. 5-5 SIMS profile of STO/TaN with or without N^+ treatment on the lower TaN.

Fig. 5-6 (a) The XRD spectra of STO after a 400-450°C O_2 PDA. Crystallization of STO was found at 450°C O_2 PDA. (b) Cross-sectional TEM of STO/ N^+ -treated-TaN with an enlarged STO image in (c).

Fig. 5-7 $\Delta C/C$ - V characteristics for STO MIM capacitors and the dependence on (a) plasma-nitridation on the lower TaN and (b) different capacitance densities of 28 to 49 fF/ μm^2 (c) Frequency dispersion of the 28 fF/ μm^2 density capacitor.

Fig. 5-8 (a) Temperature-dependent normalized capacitance for MIM capacitors with or without plasma-nitridation of the lower TaN. (b) The α , TCC and CET as a function of various treated MIM capacitors.

Fig. 5-9 $\Delta C/C$ - $1/C$ plot of TaN/STO/TaN and various high- κ MIM capacitors. The exponential decrease with increasing $1/C$ is important for designing capacitors for different applications.

Chapter 6 Very High Density (44fF/ μm^2) SrTiO₃ MIM Capacitors for RF Applications

Fig. 6-1 (a) C - V and (b) J - V characteristics of STO MIM capacitors. The C - V results from 100 kHz to 1 MHz are measured from LCR meter and the data from 0.2 GHz to 10 GHz are obtained from the S-parameters. High capacitance

density of 44 and 49 fF/ μm^2 were measured with low leakage density of 5×10^{-7} and 6×10^{-6} A/cm².

Fig. 6-2 Measured and simulated J - $E^{1/2}$ of STO MIM capacitors.

Fig. 6-3 (a) Measured and simulated two-port S-parameters for STO MIM capacitors, from 500 MHz to 10 GHz and (b) equivalent circuit model for capacitor simulation in RF regime.

Fig. 6-3 (a) Frequency dependent capacitance density, $\Delta C/C$ and α for a STO MIM capacitor biased at 1.5V. The data for frequencies >1 MHz were obtained from the S-parameters. (b) The $\Delta C/C$ - V characteristics of a STO MIM capacitor at RF regime.

Fig. 6-4 (a) Q-factor of TaN/STO/TaN MIM capacitors biased at 1.5V (b) The temperature-dependent normalized capacitance (TCC) with different frequency. The capacitor size is $20 \mu\text{m} \times 20 \mu\text{m}$.

Chapter 7 Use of a High Work-Function Ni Electrode to Improve the Stress Reliability of Analog SrTiO₃ Metal-Insulator-Metal Capacitors

Fig. 7-1 J - V characteristics of [Ni or TaN]/STO/TaN capacitors, measured at 125°C.

The inserted figure is the band alignment of the STO MIM device with TaN or Ni as the upper electrode.

Fig. 7-2 (a) C - V characteristics of [Ni or TaN]/STO/TaN capacitors before and after

different voltage stress at 25°C. (c) C - V characteristics of Ni/STO/TaN capacitors before and after constant-voltage stress at 25 and 125°C.

Fig. 7-3 $\Delta C/C$ - V characteristics of MIM capacitors with Ni, and with TaN electrodes.

Fig. 7-4 (a) The $\Delta C/C$ vs. stress voltage for a 10 year reliability period (b) The $\Delta C/C$ values for 10 year-stress were obtained from the figure of the extrapolated $\Delta C/C$ vs. stress time to 10 years.

Fig. 7-5 Temperature dependences of V_{CC} α and normalized capacitance with Ni and TaN electrode.

Table Caption

Chapter 2 High- κ Ir/TiTaO/TaN Capacitors Suitable for Analog IC Applications

Table 2-1 Comparison of various high- κ capacitors. All the requirements of the ITRS roadmap at 2018 are satisfied by the Ir/TiTaO/TaN capacitor.

Chapter 4 Thermal Leakage Improvement by Using a High Work-Function Ni Electrode in High- κ TiHfO MIM Capacitors

Table 4-1 Comparison of important device data for MIM capacitors with various high- κ dielectrics and work-function metals.

Chapter 5 High Performance SrTiO₃ Metal-Insulator-Metal Capacitors for Analog Applications

Table 5-1 Comparison of various high- κ capacitors. The TaN/STO/TaN capacitor shows the best performance, exceeding the requirements of the ITRS roadmap for 2018.